# STEAM-THERMAL RECYCLING OF TIRE SHREDS: CALCULATION OF THE RATE OF EXPLOSION-PROOF FEED OF STEAM

**V. A. Kalitko**     UDC 536.246.2

*Consideration has been given to the process of steam-thermal recycling (steam thermolysis) of car-tire shreds in the mechanical worm-type reactor with a steam superheater and intrinsic utilization steam generation on the waste combustion products; the process was developed at the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus and was put into trial-commercial operation in Taiwan. The combustible properties of the pyrogas and the specific feed of steam for the explosion proofness of the process have been determined on the basis of the balance model of ignition of fuel gases and the existing indices of the yield of thermolysis products in the form of pyrogas.*

**Introduction.** Thermal recycling (pyrolysis or thermolysis) of car-tire shreds is a well-known and very promising solution of the problem of their utilization for production of mazut, liquid fuel, and casinghead fuel gas and of commercial carbon as a solid product — the residue of recycling after the separation of steel chord. This technology is a top priority for a number of industrial plants and scientific centers in different countries, including the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, where the process of steam thermolysis of such shreds has been developed and is being improved [1–7]. The superheated steam serves as an additional factor of heating of tires directly from within the thermolysis reactor, intensifying the process and ensuring such advantages as reduction in the content of sulfur in the fuel condensate and increase in the explosion proofness of the pyrogas in the reactor.

In a number of countries (the USA, China, Taiwan, and others), where industrial shredding and separation of tires from the steel chord for their utilization in highway engineering have been launched, such a recycling is carried out in different mechanical reactors (of the worm or barel type) in which the process is intensified by mere mixing of the shredded rubber without steam [8–12]. To build on the above advantages, the process of steam thermolysis of the tire shreds in a steam worm-type reactor and the corresponding equipment have been developed at the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus; two complexes of this equipment with an output of 1000 kg/h each complete with their steam utilizer boiler and a unit of three pipe condensers for separating the fractions of mazut, fuel, and steam condensate were supplied to Taiwan and were put into operation there in 2007.

As far as the specific yield of products per 1 kg of the recycled material is concerned, this process is not fundamentally different from other such technologies and involves mainly checking and development of the adopted designs of the furnace, the reactor, condensers, and others. The efficiency of steam feed manifested itself not only as the intensification and improvement of safety but also as the control of the process where increase in the feed of steam combined with its utilization generation and superheating quite efficiently and dynamically reduces the temperature in the reactor. And conversely, on reduction in the steam feed, we observed an increase in the temperature and a shift of the thermolysis process toward gasification, which is manifested as a reduction in the yield of the fuel condensate and a larger yield of the noncondensed casinghead gas. Furthermore, steam considerably reduces the partial pressure and the condensation temperature of the pyrogas for extraction of the above fractions of fuel compared to their existing values. Finally, steam is efficient merely as a heat-transfer agent for preheating and feed of the pyrogas to condensers, since this gas is much heavier than air and is characterized by a high concentration of soot carbon.

781

An important factor in carrying out the process is the circulating system of feed water of the boiler with return of the steam condensate via a sedimentation basin to separate the residual fuel inclusions; without this system, steam thermolysis involves large volumes of the waste of such a condensate whose water is light brown and has a light aroma of damp rubber. As applied to the steam utilizer boiler developed by the "Head Specialized Design Office" Public Corporation (Brest) and generating steam on the waste gases of the reactor's heating chamber, such deviations from the standards of feed water, as far as the organic composition of the condensate is concerned, have no effect on the boiler operation. The specific generation of steam is to 0.5 kg per 1 kg of the recycled material or 0.2 kg per 1 $nm^3$ of the waste gases as the products of burning of the condensed fuel or afterburning of the casinghead fuel gas.

However, we clearly see such a fundamental drawback of steam thermolysis as a loss of no less than 540 kcal/kg of heat by steam condensation, whereas the thermolysis of tires requires no more than 300 kcal/kg. From this viewpoint, one should minimize the use of steam and primarily its demand to ensure the explosion proofness of the process, which amounts to no less than 85% of the mass of steam mixed with pyrogas (or 5.66 kg of steam per 1 kg of pyrogas, ratio 85:15), according to the data of [3]. No less that 3 kg of the steam feed per 1 kg of the initial tire feed is required for a yield of to 45% of the fuel condensate and 10% of the noncondensated casinghead gas, i.e., per 55% of the pyrogas mass, on the whole. In the present work, we have made an effort to analytically substantiate this index with allowance for thermal conditions and for the combustible properties of the pyrogas, using the balance model of its ignition on the basis of combustion activation energy for this purpose.

**Calorimetric Properties of the Pyrogas.** First we determine the calorimetric content of the pyrogas in the reactor; the calorimetric content, at a nearly atmospheric pressure, is considered as the sum of the heat of combustion of a condensed fuel and a noncondensable casinghead fuel gas in their known proportion of the yield per 1 kg of tires. For the above technologies of recycling with steam and without steam, this is characterized as follows: $Q_{oil} \approx 41$ MJ/kg is the heat of combustion of the fuel obtained in steam thermolysis [1–7], $Q_{oil} \approx 18,000$ BTU/lb $\approx 42$ MJ/kg is the same, for the fuel in thermolysis without steam [8–12], $Q_{gas} \approx 19$ MJ/kg is the heat of combustion of the casinghead gas in steam thermolysis [1–7], $Q_{gas} \approx 1200$ BTU/$ft^3 \approx 39$ MJ/$m^3$ is the same, for the casinghead gas without steam [8–12], OIL = 40–45% is the yield of the fuel condensate in steam thermolysis of whole tires [1–7], OIL = 50–55% is the fuel yield in steam-free thermolysis of tire shreds [8–12], GAS $\approx$ 10–20% is the yield of the noncondensed casinghead gas according to [1–7], and GAS $\approx$ 10% is the approximate yield of the noncondensed casinghead gas according to [8–12].

The different indices of the yield and heat of combustion of the casinghead gas from [1–7] and [8–12] correlate quite well when it is taken into account that, in steam technology, the steam itself partially does not condense together with the casinghead gas, diluting the gas nearly twofold. In particular, at a temperature of 75–80$^o$C and a 100% relative humidity in the steam condenser (condition of any condensation), the residual content of steam in the casinghead gas, which amounts to 50–55%, is usually determined by analogy with calculation of the content of steam in air. As applied to the composition of the pyrogas in the reactor, the calorific value of the casinghead gas is taken according to [8–12], since its dilution with steam occurs in the condenser once it has escaped from the reactor:

$$Q_{pgas(1kg)} = \frac{OIL}{100} Q_{oil} + \frac{GAS}{100} Q_{gas}, \quad Q_{pgas(1kg)} = 0.45 Q_{oil} + 0.1 Q_{gas} = 0.45 \cdot 42 + 0.1 \cdot 39 = 22.8 \text{ MJ/kg}.$$

Whereas the casinghead gas mainly consists, accordingly to all the available data [1–12], of approximately equal parts of the aromatic mixture of butadiene $C_4H_6$ and pentane $C_5H_{12}$, the fuel condensate [13] consists predominantly of a mixture of terpenes $(C_5H_8)_{n=2,3,4}$. Knowing the molecular weights of these gases ($\mu_1 = 54$ for butadiene, $\mu_2 = 70$ for pentane, and $\mu_3 = 136$ for isoterpene $C_{10}H_{16}$ as the most light-weight and dominant one of the pyrogas terpenes), we can determine their densities in the reactor at 350–400$^o$C as follows: $\mu_{gas} = \frac{\mu_1 + \mu_2}{2} = 62$ is the mean molecular weight of the casinghead gas, $\rho_{gas(1,2)} = \frac{\mu_{gas}}{V_A} \frac{273}{623} = 1.224$ kg/$m^3$ is the density of the casinghead gas, and $\rho_{gas(3)} = \frac{\mu_3}{V_A} \frac{273}{623} = 2.79$ kg/$m^3$ is the density of isoterpene.

The density of the pyrogas is determined as the partial sum of the densities

782

TABLE 1. Comparative Indices and Results of the Computational Model

| Fuel gases | $E$ [14] | | $K_{\max}$, % [15] | $V_{a(\min)}$, m³/m³ | $T_{\text{ign}}$, °C | |
| --- | --- | --- | --- | --- | --- | --- |
| | kJ/kmole | kJ/nm³ | | | [15] | (3) |
| Methane $CH_4$ | 103, 800 | 4675 | 15.0 | 6.0 | 545—800 | 585 |
| Pentane $C_5H_{12}$ | 146, 000 | 6575 | 8.0 | 11.5 | 285—510 | 440 |

$$\rho_{\text{pgas}} = \frac{\text{GAS}}{\text{GAS} + \text{OIL}}\,\rho_{\text{gas}(1,2)} + \frac{\text{OIL}}{\text{GAS} + \text{OIL}}\,\rho_{\text{gas}(3)} = \frac{10}{10 + 45}\,1.224 + \frac{45}{10 + 45}\,2.79 = 2.5 \text{ kg/m}^3 .$$

The volume of formation of the pyrogas in the reactor per 1 kg of the recycled material is

$$V_{\text{pgas}(1\text{kg})} = \frac{\text{OIL} + \text{GAS}}{100\rho_{\text{pgas}}} = \frac{45 + 10}{100 \cdot 2.5} = 0.22 \text{ m}^3/\text{kg} .$$

The calorimetric content of 1 m³ of the pyrogas in the reactor is

$$Q_{\text{pgas}(1\text{m}^3)} = \frac{Q_{\text{pgas}(1\text{kg})}}{V_{\text{pgas}(1\text{kg})}} = \frac{22.8}{0.22} = 103.6 \text{ MJ/m}^3 .$$

The result obtained minus the component of the casinghead gas in terms of the pyrogas mass is quite consistent with the heat of combustion of the fuel as the condensate of the same mass

$$Q_{\text{pgas}(1\text{kg})} = \frac{Q_{\text{pgas}(1\text{m}^3)} - \text{GAS}\,Q_{\text{gas}}}{\rho_{\text{pgas}} - \text{GAS} \cdot \rho_{\text{pgas}}} = \frac{103.6 - 0.1 \cdot 39}{2.5 - 0.1 \cdot 1.224} = 41.9 \text{ MJ/kg} .$$

**Steam for Explosion Proofness of the Pyrogas.** We consider a continuous and steady-state process in which the feed of steam, the charging and discharging of the reactor, and the chemical composition of the pyrogas in it are stable with time, which is characteristic precisely of mechanical thermolysis reactors, since in chamber batch reactors, cyclic changes in the composition, temperature, density, and other parameters of the pyrogas are inevitable. Let us use the notion of activation energy [14] from the kinetics of chemical reactions, including combustion reactions, and direct our attention to the balance model of ignition of gases; the activation energy for this model can be interpreted in the first approximation as heating 1 kmole of the gas to the temperature of its ignition under the conditions of the minimum volume of mixing with air sufficient for this purpose:

$$E = c_{p(\text{a})}\left(1 + V_{(\text{a})\min}\right)\left(T_{\text{ign}} - T_{\text{a}}\right) . \tag{1}$$

The model becomes clearer if we express the minimum volume of air for explosive ignition of 1 nm³ of the gas by the known value of the upper concentration limit of this ignition [15]

$$V_{(\text{a})\min} = \frac{1}{K_{\max}} - 1 , \tag{2}$$

and next determine the ignition temperature from (1) and (2); for this purpose we refer to the activation energy of 1 nm³ of the gas, dividing it by the Avogadro number (22.2 nm³/kmole), and allow that the specific heat of the gas-air mixture is determined predominantly by the air under the assumption of a large air volume:

$$T_{\text{ign}} = T_{\text{a}} + \frac{E}{c_{p(\text{a})}\left(1 + V_{(\text{a})\min}\right)V_{\text{A}}} = T_{\text{a}} + \frac{E K_{\max}}{c_{p(\text{a})}V_{\text{A}}} . \tag{3}$$

Table 1 gives a comparative result of calculation from this model using methane and pentane as some of the most light-weight and heavy-weight fuel hydrocarbon gases as an example.

Without assuming special inhibitor properties of steam, we determine the explosion-proof volume of its feed per 1 m³ of the pyrogas on the basis that steam dilutes the pyrogas in an inertial manner and the activation energy from (1) is no longer sufficient for heating this more heat-intensive gas-air mixture with steam to the ignition temperature (3). Allowing for the dominant content of steam in the mixture and using the specific heat of the former and the pyrolysis temperature as the initial heating temperature, i.e., $T_{pyro}$ instead of $T_a$, we can formulate the conditions of ignition of the pyrogas mixed with steam in the form

$$E = c_{p(s)} \left(1 + V_{(a)min} + V_{s(1m^3)}\right) \left(T_{ign} - T_{pyro}\right). \tag{4}$$

The sought volume of steam feed per 1 m³ of the pyrogas is determined from (1)–(4):

$$V_{s(1m^3)} = \left(1 + V_{(a)min}\right) \left[\frac{c_{p(a)}}{c_{p(s)}} \frac{T_{ign} - T_a}{T_{ign} - T_{pyro}} - 1\right]. \tag{5}$$

Further calculation from (5) requires determination of the minimum air volume necessary for igniting 1 m³ of the pyrogas, the reference data on the upper concentration limit of ignition and explosiveness for which are still lacking, which makes it impossible to use relation (2). We use a value (known from practice) of approximately 1 nm³ of the reduced flow rate of air per 3800 kJ of the heat release of different organic fuels and gases [14], from which the normal air volume for combustion of 1 nm³ of the pyrogas can be determined as follows:

$$V_{a(1m^3)} \approx \frac{Q_{pgas(1m^3)}}{3800}. \tag{6}$$

Considering the pyrogas as the mixture of heavy hydrocarbons (butanes, pentanes, terpenes, and others) for which the upper concentration limit of ignition, according to the reference data [15], is 2.5–2.75 times higher than its normal stoichiometric concentration with air, we assume that the minimum air volume for ignition of the pyrogas must also be definitely 2.75 times lower than that required for normal combustion from (6):

$$V_{(a)min} \approx \frac{Q_{pgas(1m^3)}}{2.75 \cdot 3800} = \frac{Q_{pgas(1m^3)}}{10\,450}. \tag{7}$$

From expressions (5)–(7), we obtain the calculated formula which, for the above pyrolysis conditions $T_a = 20^oC$, $T_{pyro} = 350^oC$, $T_{ign} = 440^oC$, $c_{p(a)} = 1.25$ kJ/(nm³·°C), and $c_{p(s)} = 0.86$ kJ/(nm³·°C) yields the following result:

$$V_{s(1m^3)} = \left(1 + \frac{Q_{pgas(1m^3)}}{10\,450}\right) \left[\frac{c_{p(a)}}{c_{p(s)}} \frac{T_{ign} - T_a}{T_{ign} - T_{pyro}} - 1\right] \approx 64 \ \ m^3/m^3. \tag{8}$$

**Steam Feed per 1 kg of the Recycled Material.** This result in the form of the volume of feed of a superheated steam per 1 m³ of the pyrogas cannot serve as the technological index of the process, since this parameter is not measured directly and is not the index of recycling. Conversion to 1 kg of the tire feed is carried out as follows: $\rho_s = 0.412$ kg/m³ is the steam density in the reactor at atmospheric pressure, $\rho_{pgas} = 2.5$ kg/m³ is the pyrogas density obtained above under the same conditions, $G_{s(1kg)} = \frac{\rho_s}{\rho_{pgas}} V_{s(1m^3)} = \frac{0.412}{2.5} 64 = 10.5$ kg/kg is the steam feed per 1 kg of the pyrogas, PGAS = OIL + GAS = 10% + 45% = 55% is the percent of feed mass as the pyrogas, and $G_s/G_{tire} = 0.55 G_{s(1kg)} = 0.55 \cdot 10.5 = 5.77$ kg/kg is the steam feed per 1 kg of the tire feed.

**Conclusions.** The result obtained is nearly twice as large as the initial prerequisite in the form of 3 kg of steam per 1 kg of tires from [3], which, probably can be explained by the increased temperature of pyrolysis and the pyrogas itself in the reactor compared to the regular (normal) thermal conditions of determination of explosive concen-

trations of gases in air. In the absence of direct experimental data for this concentration of the pyrogas with steam, indirect confirmation of the calculated value obtained is the so-called minimum calorific value of ignition and combustion of generator gases in air (previously known from the practice of pyrolysis and gasification of solid fuels) [16]

$$Q_{\text{pgas(min)}} \approx 950 \text{ kcal/nm}^3 \approx 4 \text{ MJ/nm}^3 \,,$$

which is approximately the same for the normal density of such gases within 0.9–1.1 kg/nm$^3$ in terms of mass.

It is difficult to assume what will be more rapid and probable in the case of hypothetical access of the external air to the reactor: cooling and condensation of the pyrogas followed by the explosive ignition of the residual gas or ignition of the entire initial mass of the pyrogas at once. Considering the last variant as being quite realistic and the most hazardous, on converting the resulting heat of combustion of the pyrogas to the entire mass of its diluted mixture with steam, we obtain the same minimum calorific value of ignition:

$$Q_{\text{pgas(min)}} = \frac{Q_{\text{pgas}}}{\rho_{\text{pgas}} G_{\text{s(1kg)}}} = \frac{103.6}{2.5 \cdot 10.5} = 3.95 \text{ MJ/kg} \,.$$

## NOTATION

$c_{p(\text{s})}$ and $c_{p(\text{a})}$, specific heats of the steam and air respectively, kJ/(nm$^3 \cdot {}^{\text{o}}$C); $E$, activation energy, kJ/kmole; $G_{\text{tire}}$ and $G_{\text{s}}$, shred feed and steam feed respectively, kg/h; $G_{\text{s(1kg)}}$, steam feed per 1 kg of the pyrogas; $K_{\text{max}}$, upper concentration limit of ignition and explosiveness of fuel gases; $Q_{\text{oil}}$, specific heat of combustion of the liquid fuel, MJ/kg; $Q_{\text{gas}}$ and $Q_{\text{pgas(1m}^3)}$, heat of combustion of 1 nm$^3$ of the volume of the casinghead gas and the pyrogas respectively, MJ/m$^3$; $Q_{\text{pgas(1kg)}}$, heat of combustion of 1 kg of the pyrogas mass, MJ/kg; $T_{\text{pyro}}$, $T_{\text{ign}}$, and $T_{\text{a}}$, temperatures of pyrolysis, ignition of the pyrogas, and the ambient air respectively, $^{\text{o}}$C; $V_{\text{pgas(1kg)}}$, volume of formation of the pyrogas per 1 kg of recycled tires, m$^3$/kg; $V_{\text{a(min)}}$, minimum air volume for ignition of 1 nm$^3$ of the gas, nm$^3$/nm$^3$; $V_{\text{s(1m}^3)}$, volume of explosion-proof feed of steam per 1 m$^3$ of the pyrogas, m$^3$/m$^3$; $V_{\text{A}}$, 22.4 nm$^2$/kmole, Avogadro number for gases; $\mu_{\text{gas}}$ and $\mu_{\text{pgas}}$, molecular weight of the casinghead gas and the pyrogas respectively; $\rho_s$, $\rho_{\text{gas}}$, and $\rho_{\text{pgas}}$, density of the steam, the casinghead gas, and the pyrogas respectively, kg/m$^3$. Subscripts: a, air; gas, fuel gas; ign, ignition; max, maximum; min, minimum; oil, fuel; pgas, pyrogas; pyro, pyrolysis; s, steam; tire, tires.

## REFERENCES

1. V. N. Drozdov, D. V. Aristarkhov, and N. N. Egorov, Modeling of the technological processes of thermal steam processing of rubber waste, in: *Proc. 4th Minsk Int. Forum "Heat and Mass Transfer–MIF-2000,"* 22–26 May 2000, Minsk (2000), pp. 100–103.
2. D. V. Aristarkhov, N. N. Egorov, G. I. Zhuravskii, et al., *Steam Thermolysis of Organic Waste* [in Russian], ITMO NAN Belarusi, Minsk (2001).
3. D. V. Aristarkhov and G. I. Zhuravskii, Modeling of the vapor thermolysis of rubber waste, *Inzh.-Fiz. Zh.*, **74**, No. 6, 146–151 (2001).
4. D. V. Aristarkhov, G. I. Zhuravskii, É. P. Polesskii, and B. A. Permyakov, Technologies of vegetable-biomass, technical-rubber, and plastic-waste processing, *Inzh.-Fiz. Zh.*, **74**, No. 6, 152–155 (2001).
5. G. I. Zhuravskii and V. A. Sychevskii, Calculation of the thermolysis of rubber-tire shreds, in: O. G. Martynenko (Ed.), *Heat- and Mass Transfer*, Collec. Scient. Papers, Minsk (2002), pp. 13–20.
6. G. I. Zhuravskii and V. A. Sychevskii, Numerical calculation of vapor thermolysis of organic waste, *Inzh.-Fiz. Zh.*, **76**, No. 6, 104–109 (2003).
7. G. I. Zhuravskii, A. S. Matveichuk, and P. L. Falyushin, Obtaining fuel based on products of organic-waste steam thermolysis, *Inzh.-Fiz. Zh.*, **78**, No. 4, 58–62 (2005).
8. Patent U.S. 5720252, F23G 5/12, 24.02.1998. *Method and Apparatus for Recovering Constituents from Discarded Tires.*
9. Patent U.S. 5735948, C04B 24/00, 07.04.1998. *Process for Co-Recycling Tires and Oils.*

10. Yang Yongrong, Chen Jizhong, Zhao Guibin, Technical advance on the pyrolysis of used tires in China, in: *Proc. China–Japan Int. Academic Symp.: Environmental Problem in Chinese Iron-Steelmaking Industries and Effective Technology Transfer*, Sendai, Japan, 6 March 2000.

11. Patent U.S. 6657095 B1, C10G 1/10, 02.12.2003. *Continuous Temperature Variance Pyrolysis for Extracting Products from Tire Chips*.

12. Patent U.S.6736940 B2, C10B 51/00, 18.05.2004. *Process for Pyrolizing Tire Shreds and Pyrolysis Systems*.

13. I. A. Rozhnovskii, *Thermal Technologies of Processing Organic Waste* [in Russian], Yunipak, Minsk (2005).

14. V. V. Pomerantsev, K. M. Aref'ev, D. B. Akhmedov, et al., *Foundations of Practical Theory of Combustion* [in Russian], 2nd rev. and augm. ed., Energoatomizdat, Moscow (1986).

15. N. P. Staskevich, G. N. Severinets, and D. Ya. Vigdorchik, *Handbook of Gas Supply and Use of Gas* [in Russian], 2nd rev. and augm. ed., Nedra, Leningrad (1990).

16. D. B. Ginzburg, *Solid-Fuel Gasification* [in Russian], Gosstroizdat, Moscow (1958).